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OHAMA TORU**(54) REMOVAL OF RESIDUAL MONOMER FROM RESIN BY EVAPORATION****(57)Abstract:**

**PROBLEM TO BE SOLVED:** To provide a method for removing, by evaporation, a residual monomer from a specific resin in a short time without deteriorating its quality by mixing the resin with water or steam under specific conditions and keeping the mixture under a vacuum.

**SOLUTION:** This method mixes (A) a resin comprising (i) a resin produced by polymerization of a vinyl-based monomer, as the essential ingredient, (ii) a resin other than the component (i), e.g. epoxy or polyester resin, as required, and (iii) an organic solvent, e.g. xylene or toluene with (B) water or steam, injected in the component A at 120 to 200° C, while keeping the mixture preferably under a pressure of 1 to 10 kg/cm<sup>2</sup>G preferably for 3 to 120 min, and then removing the residual monomer from the component A preferably to 200 ppm or less by evaporation preferably under a pressure of 5 to 50 Torr. It is preferable to heat the polymerized component A, prior to injecting the component B under a pressure, to distill off volatiles under the normal pressure or vacuum to 3 wt.%.

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CLAIMS

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## [Claim(s)]

[Claim 1] The devolatilization approach of the residual monomer characterized by to include the process which changes into a reduced-pressure condition and devolatilizes after pressing water or a steam fit into resin and mixing in the state of pressurization at 120–200 degrees C in the approach of carrying out devolatilization reduction of the residual monomer content in the resin (A) which uses as an indispensable component the resin (a) obtained by carrying out the polymerization of the vinyl system monomer.

[Claim 2] The devolatilization approach according to claim 1 of maintaining a pressurization condition for 3 – 120 minutes after adding water or a steam into (A).

[Claim 3] The devolatilization approach according to claim 1 or 2 that volatile matter adds water or a steam to 3 or less % of the weight of (A).

[Claim 4] For the pressure of a pressurization condition, claims 1–3 it is [ claims ] 5 – 50Torr are [ the pressure of 1–10 kg/cm<sup>2</sup>G and a reduced pressure condition ] the devolatilization approaches of a publication either.

[Claim 5] Claims 1–4 which are resin with which (a) carries out the polymerization of the vinyl system monomer which makes a subject styrene and/or (meta) acrylic-acid alkyl ester, and is obtained are the devolatilization approaches of a publication either.

[Claim 6] Claims 1–5 whose residual monomer contents in (A) after devolatilization are 200 ppm or less are the devolatilization approaches of a publication either.

[Claim 7] Claims 1–6 whose (A) is a toner binder for electrophotography are the devolatilization approaches of a publication either.

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**DETAILED DESCRIPTION**

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**[Detailed Description of the Invention]****[0001]**

**[Field of the Invention]** This invention relates to the devolatilization approach of the residual monomer in resin. It is related with the approach of devolatilizing effectively the unreacted monomer which remains in more detail in the resin obtained by carrying out the polymerization of the vinyl system monomers, such as a toner binder for electrophotography, for a short time.

**[0002]**

**[Description of the Prior Art]** In the toner binder for electrophotography using the resin obtained by carrying out the polymerization of the vinyl system monomer etc., if an unreacted vinyl system monomer etc. remains, at the time of heating melting, an odor will be emitted, and displeasure will be given, and the problem of being harmful to the body will be caused. As an approach of carrying out devolatilization removal of the unreacted vinyl system monomer which remains in resin, it is the approach of removing as a reduced pressure condition at polymerization temperature or the temperature beyond it after \*\* polymerization termination.

\*\* How to blow and remove inert gas etc. in the system maintained to polymerization temperature or the temperature beyond it after polymerization termination.

\*\* How to remove the obtained resin under reduced pressure using an extruder etc.

Generally \*\*\*\* is performed.

**[0003]**

**[Problem(s) to be Solved by the Invention]** However, a process not only takes long duration to these approaches, but they had the problem which causes the debasement of resin by the open polymerization by the elevated temperature etc. Moreover, when it was going to remove the unreacted monomer etc., without starting the debasement of resin using the conventional approach, the limitation reduced the amount of survival of an unreacted monomer to about at most 500 ppm.

**[0004]**

**[Means for Solving the Problem]** Artificers reached this invention, as a result of examining wholeheartedly how to remove a residual monomer for a short time, without starting the debasement of resin. That is, this invention is the devolatilization approach of the residual monomer characterized by to include the process which changes into a reduced-pressure condition and devolatilizes in the approach of carrying out devolatilization reduction of the residual monomer content in the resin (A) which uses as an indispensable component the resin (a) obtained by carrying out the polymerization of the vinyl system monomer, after pressing water or a steam fit into resin and mixing in the state of pressurization at 120–200 degrees C.

[0005] The resin (A) with which the approach of this invention is applied uses as an indispensable component the resin (a) obtained by carrying out the polymerization of the vinyl system monomer. As a vinyl system monomer which constitutes (a), halogen content vinyl system monomers, such as vinyl ester, such as styrene (styrene, alpha methyl styrene, etc.), an acrylic acid (meta) and its ester, acrylonitrile (meta), and vinyl acetate, and a vinyl chloride, etc. are raised. Styrene, an acrylic acid (meta), and its ester are used preferably among these.

[0006] (A) An epoxy resin, polyester resin, xylene resin, and polyolefine may be contained in inside with (a).

Moreover, organic solvents, such as a xylene and toluene, may be contained.

[0007] \*\* (a) is obtained by well-known polymerization methods, such as solution polymerization and a bulk polymerization. Moreover, the amount of the residual monomer in the resin after polymerization reaction termination is usually 0.5 – 20 % of the weight.

[0008] The devolatilization approach of this invention consists of a process of the following \*\* – \*\*.

\*\* . Process distilled out until it heats the resin after polymerization termination and becomes 3 or less % of the weight about volatile matter in the state of ordinary pressure or reduced pressure.

\*\* . Process which presses water or a steam fit into resin, maintains a pressurization condition, and is mixed.

\*\* . Process which carries out subsequently to a reduced pressure condition, and devolatilizes by maintaining a reduced pressure condition.

Process \*\* and \*\* are usually repeated 1 to 4 times preferably 0 to 5 times.

[0009] 130–200 degrees C whenever [ stoving temperature / of the resin in a devolatilization process ] is usually 140–180 degrees C preferably. At less than 130 degrees C, the viscosity of resin becomes [ temperature ] high, if stirring becomes difficult and exceeds 200 degrees C, disassembly (open polymerization etc.) of resin will take place and quality will be reduced.

[0010] The volatile matter of the resin at the time of process \*\* termination is usually 1 or less % of the weight preferably 3 or less % of the weight. When volatile matter exceeds 3 % of the weight, it needs many counts of a repeat of process \*\* and process \*\*, the debasement of resin is imitated the compaction effectiveness of devolatilization time amount is not not only acquired, but, and it is \*\*.

[0011] The pressure in process \*\* is usually 3-8 kg/cm<sup>2</sup>G preferably 2 G one to 10 kg/cm. Less than [ 1 kg/cm<sup>2</sup>G ], water or a steam is not enough mixed for a pressure in resin, but devolatilization time amount becomes long. Moreover, even if it exceeds 10 kg/cm<sup>2</sup>G, the devolatilization effectiveness does not improve. What is necessary is for there to be especially no limitation about the amount of the water used or a steam, and just to adjust so that the above-mentioned conditions may be fulfilled.

[0012] In process \*\*, the time amount which maintains a pressurization condition is usually 15 - 60 minutes preferably for 3 to 120 minutes. This time amount becomes inadequate [ the devolatilization effectiveness ] in less than 3 minutes. On the other hand, even if it exceeds 120 minutes, the devolatilization effectiveness does not improve.

[0013] The pressure of the reduced pressure condition in process \*\* is usually 10 - 40Torr preferably five to 50 Torr. If a large-scale decompression device is needed and 50Torr is exceeded in order to make it less than 5 Torrs, devolatilization time amount becomes long, imitates the debasement of resin, and comes and is not desirable. The time amount which maintains a reduced pressure condition is usually 15 - 120 minutes.

[0014] The content of the residual monomer in the resin devolatilized by the approach of this invention is usually 200 ppm or less, and can also be referred to as 100 ppm or less by choosing desirable conditions.

[0015]

[Example] Hereafter, although an example explains this invention further, this invention is not limited to this. In addition, % shows weight % below.

[0016] The equipment, conditions, and approach which were used for measurement are as follows.

The [approach of the quantum of a residual monomer] Equipment : Shimadzu gas chromatograph SIMAZU GC-14A column : PEG 20M 20% Chromosorb W MESH 60 - 80 column temperature : 100-degree-C injection temperature: 180 degree-CN2 quantity of gas flow: It is the sample solution by 40ml/. : 5% of dimethylformamide solution solution injection rate: 1microl detector : To the FID standard substance The calibration curve was created using alpha-methyl styrene and the residual monomer content was calculated.

[The measuring method of volatile matter]

Equipment : Drier of the \*\* style (product made from TABAI)

The samples 1.5-2.0g ground on 20-mesh pass were weighed precisely, after putting on the 150-degree C dryer of the \*\* style gently for 45 minutes, it took out, and desiccation residue was weighed precisely, and it asked by the following formula.

Volatile-matter (%) = (1-desiccation residue weight / sample weight) x100 The [approach of measurement of a weight average molecular weight and number average molecular weight (polystyrene criterion)] Equipment : HLC-802A (product made from Oriental soda)

Column : Column TSK gel GMH6 Two (product made from Oriental soda)

Sample solution: 0.5% of THF solution solution injection rate: 20microl detection equipment: Refractive index detector

[0017] After teaching xylene 64kg into example 1 cooling pipe and a 1000l. reaction vessel with a double helical ribbon agitator (it is henceforth called a reaction vessel 1), heated at 200 degrees C, and it was dropped into it, having covered [ styrene 400kg and / 12.1kg ] them for 3 hours, it was made to react at this temperature further for 1 hour, and 476.1kg (a-1) of xylene solutions of the resin (p-1) of weight average molecular weight 4200 was obtained. Having kept whenever [ system internal temperature ] at 60 degrees C, and stirring it, after adding xylene 80kg to \*\* (a-1), styrene / 171.4kg (a-2) of granular acrylic-acid n-butyl (weight ratios 80/20) copolymers of the weight average molecular weight 850,000 obtained by the suspension-polymerization method were thrown in over 1 hour, and it dissolved in homogeneity. Next, nitrogen gas permuted the inside of a reaction vessel 1, and the temperature up was carried out to 180 degrees C by ordinary pressure, and it changed into the reduced pressure condition, maintaining temperature subsequently to 180 degrees C, volatile matter was distilled out, and resin (A-1) was obtained. The volatile matter of this thing was 0.9%. Subsequently, the inside of a tub was made sealing, and it pressed fit until the steam was set to 5 kg/cm<sup>2</sup>G into \*\* (A-1). Under stirring, the reduced pressure condition was maintained after maintaining the pressurization condition for 30 minutes until the pressure was set to 20Torr(s). This steam installation and actuation of reduced pressure were repeated 3 times, and resin (P-1) was obtained. The time amount required by ejection had been 5 hours since it began to have added a steam. The content of a residual monomer (styrene) was 60 ppm.

[0018] After teaching xylene 64kg into example 2 reaction vessel 1, it heats at 200 degrees C. At one of the two of 40kg (PE-1) of polyester resin of number average molecular weight 2500, and the end of (PE-1) obtained by styrene 342.4kg in it by the polycondensation of a terephthalic acid and the two mol addition product of bisphenol A ethyleneoxides, methacryloyl isocyanate The mixture and 9.4kg of di-t-butyl peroxide in which 17.2kg (PE-2) of reaction \*\*\*\* polyester resin was dissolved are dropped over 3 hours. It was made to react at this temperature furthermore for 1 hour, and 473kg (a-3) of xylene solutions of the resin (p-2) of weight average molecular weight 4200 was obtained. Having kept whenever [ system internal temperature ] at 60 degrees C, and stirring it, after adding xylene 80kg into \*\* (a-3), 171.4 (a-2)kg was supplied over 1 hour, and it dissolved in homogeneity. Next, nitrogen gas permuted the inside of a reaction vessel 1, and the temperature up was carried out to 180 degrees C by ordinary pressure, and it changed into the reduced pressure condition, maintaining temperature subsequently to

180 degrees C, volatile matter was distilled out, and resin (A-2) was obtained. The volatile matter of this thing was 0.3%. Subsequently, the inside of a tub was made sealing, and it pressed fit until the steam was set to 7 kg/cm<sup>2</sup>G into \*\* (A-2). The reduced pressure condition was maintained after maintaining the pressurization condition for 40 minutes until the pressure was set to 20Torr(s). Repeat resin (P-2) was obtained for this steam installation and actuation of reduced pressure once again. The time amount required by ejection had been 3 hours since it began to have added a steam. The content of residual styrene was 70 ppm.

[0019] At 180 degrees C, the reduced pressure condition was maintained as it was, and the resin (A-1) obtained like example of comparison 1 example 1 was devolatilized. Although, as for the content of residual styrene, the devolatilization time amount in a reduced pressure condition reached 450 ppm in the 8th hour, as for the content of unreacted styrene, resin increased decomposition to 600 ppm after it in a lifting and the 13th hour.

[0020] The resin (A-1) obtained like example of comparison 2 example 1 was kept at 140 degrees C, and it devolatilized by performing reduced pressure actuation. Although the devolatilization time amount in a reduced pressure condition decreased in the 15th hour and volatile matter decreased even to 0.4%, even if it performed devolatilization actuation for 20 hours or more, volatile matter did not become 0.4% or less.

[0021]

[Effect of the Invention] It became possible to manufacture resin with few residual monomer contents extremely by the approach of this invention for a short time compared with the conventional approach, without starting debasement. Moreover, the approach of this invention is effective also as the devolatilization approaches, such as a residual monomer in manufacture of the resin which makes a subject the polymer of vinyl system monomers, such as resin used not only for the toner binder for electrophotography but for a binder and a food-grade tray.

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(54)【発明の名称】樹脂中の残存单量体の脱揮方法

(57)【要約】

【課題】 ピニル系单量体を重合して得られる樹脂を必須成分とする樹脂中に残存する未反応单量体等の揮発分を、樹脂の熱劣化をきたすことなく、短時間で効率よく脱揮除去する方法の提供。

【解決手段】 脱揮工程において、120～200℃で水もしくは水蒸気を樹脂中に圧入し加圧状態で混合した後、5～50 Torr の減圧状態で脱揮する工程を含むことを特徴とする樹脂中の残存单量体の脱揮方法。

### 【特許請求の範囲】

【請求項1】 ビニル系単量体を重合して得られる樹脂(a)を必須成分とする樹脂(A)中の残存単量体含量を脱揮低減する方法において、120～200℃で水もしくは水蒸気を樹脂中に圧入し加圧状態で混合した後、減圧状態にして脱揮する工程を含むことを特徴とする残存単量体の脱揮方法。

【請求項2】 水もしくは水蒸気を(A)中に加えた後、加圧状態を3～120分間維持する請求項1記載の脱揮方法。

【請求項3】 撥発分が3重量%以下の(A)に、水もしくは水蒸気を加える請求項1または2記載の脱揮方法。

【請求項4】 加圧状態の圧力が1～10Kg/cm<sup>2</sup>G、減圧状態の圧力が5～50Torrである請求項1～3のいずれか記載の脱揮方法。

【請求項5】 (a)がスチレン類および/または(メタ)アクリル酸アルキルエステル類を主体とするビニル系単量体を重合して得られる樹脂である請求項1～4のいずれか記載の脱揮方法。

【請求項6】 脱揮後の(A)中の残存単量体含量が200ppm以下である請求項1～5のいずれか記載の脱揮方法。

【請求項7】 (A)が電子写真用トナーバインダーである請求項1～6のいずれか記載の脱揮方法。

### 【発明の詳細な説明】

#### 【0001】

【発明の属する技術分野】本発明は、樹脂中の残存単量体の脱揮方法に関する。さらに詳しくは、電子写真用トナーバインダー等のビニル系単量体を重合して得られる樹脂中に残存する未反応単量体を短時間で効果的に脱揮する方法に関する。

#### 【0002】

【従来の技術】ビニル系単量体を重合して得られる樹脂を用いる電子写真用トナーバインダー等においては、未反応ビニル系単量体等が残存すると、加熱溶融時に臭気を発し不快感を与え、また人体に有害であるといった問題をひきおこす。樹脂中に残存する未反応ビニル系単量体等を脱揮除去する方法としては、

①重合終了後に重合温度もしくはそれ以上の温度で減圧状態として除去する方法。

②重合終了後に重合温度もしくはそれ以上の温度に維持した系内に不活性ガス等を吹き込み除去する方法。

③得られた樹脂を押出機等を用いて減圧下で除去する方法。

などが一般に行われている。

#### 【0003】

【発明が解決しようとする課題】しかしながらこれらの方法は、工程に長時間を要するだけでなく、高温による開重合等により樹脂の品質低下をきたす問題があった。

また、従来の方法を用いて、樹脂の品質低下を起こすことなく、未反応単量体等を除去しようとすると、未反応単量体の残存量をせいぜい500ppm程度まで低減するのが限界であった。

#### 【0004】

【課題を解決するための手段】発明者らは、樹脂の品質低下を起こすことなく短時間で残存単量体を除去する方法について鋭意検討した結果、本発明に到達した。すなわち本発明は、ビニル系単量体を重合して得られる樹脂(a)を必須成分とする樹脂(A)中の残存単量体含量を脱揮低減する方法において、120～200℃で水もしくは水蒸気を樹脂中に圧入し加圧状態で混合した後、減圧状態にして脱揮する工程を含むことを特徴とする残存単量体の脱揮方法である。

【0005】本発明の方法が適用される樹脂(A)は、ビニル系単量体を重合して得られる樹脂(a)を必須成分とする。(a)を構成するビニル系単量体としては、スチレン類(スチレン、α-メチルスチレン等)、(メタ)アクリル酸、およびそのエステル、(メタ)アクリロニトリル、酢酸ビニル等のビニルエステル類、塩化ビニル等のハログン含有ビニル系単量体などがあげられる。これらのうち好ましくは、スチレン、(メタ)アクリル酸およびそのエステルが用いられる。

【0006】(A)中には(a)とともに、エポキシ樹脂、ポリエステル樹脂、キシレン樹脂、ポリオレフィンが含まれていても良い。また、キシレン、トルエン等の有機溶剤が含まれていても良い。

【0007】該(a)は、溶液重合、塊状重合等の公知の重合方法により得られる。また重合反応終了後の樹脂中の残存単量体の量は、通常0.5～20重量%である。

【0008】本発明の脱揮方法は、下記①～③の工程からなる。

①. 重合終了後の樹脂を加熱し、常圧または減圧状態で揮発分を3重量%以下になるまで溜去する工程。

②. 樹脂中に水もしくは水蒸気を圧入し、加圧状態を維持し混合する工程。

③. 次いで減圧状態にし、減圧状態を維持し脱揮をおこなう工程。

工程②、③は通常0～5回、好ましくは1～4回繰り返される。

【0009】脱揮工程における樹脂の加熱温度は通常130～200℃、好ましくは140～180℃である。温度が130℃未満では、樹脂の粘度が高くなり、攪拌が困難になり、200℃を超えると樹脂の分解(開重合等)が起り品質を低下させる。

【0010】工程①終了時の樹脂の揮発分は通常3重量%以下、好ましくは1重量%以下である。揮発分が3重量%を超えると、工程②と工程③の繰り返し回数を多く必要とし、脱揮時間の短縮効果が得られないだけでな

く、樹脂の品質低下をまねく。

【0011】工程②における圧力は、通常 $1 \sim 10 \text{ kg/cm}^2$ G、好ましくは $3 \sim 8 \text{ kg/cm}^2$ Gである。圧力が $1 \text{ kg/cm}^2$ G未満では、樹脂中に水もしくは水蒸気が十分混合されず脱揮時間が長くなる。また、 $10 \text{ kg/cm}^2$ Gを超えても脱揮効果は向上しない。使用される水もしくは水蒸気の量については特に限定はなく、上記条件を満たすように調整すれば良い。

【0012】工程②において、加圧状態を維持する時間は通常 $3 \sim 120$ 分、好ましくは $15 \sim 60$ 分である。該時間が3分未満では脱揮効果は不十分となる。一方、 $120$ 分を超えても脱揮効果は向上しない。

【0013】工程③における減圧状態の圧力は通常 $5 \sim 50 \text{ Torr}$ 、好ましくは $10 \sim 40 \text{ Torr}$ である。

【残存单量体の定量の方法】

装置 : 島津製作所製ガスクロマトグラフ  
SIMAZU GC-14A  
カラム : PEG 20M 20%  
Chromosorb W MESH 60~80  
カラム温度 :  $100^\circ\text{C}$   
インジェクション温度 :  $180^\circ\text{C}$   
N<sub>2</sub>ガス流量 :  $40 \text{ ml}/\text{分}$   
試料溶液 : 5%のジメチルホルムアミド溶液  
溶液注入量 :  $1 \mu\text{l}$   
検出器 : FID

標準物質に、 $\alpha$ -メチルスチレンを用いて検量線を作成し、残存单量体含量を求めた。

【揮発分の測定方法】

装置 : 循風乾燥機（タバイ製）  
 $20$ メッシュパスに粉碎したサンプル $1.5 \sim 2.0 \text{ g}$

【量平均分子量および数平均分子量（ポリスチレン標準）の測定の方法】

装置 : HLC-802A（東洋曹達製）  
カラム : カラム TSK gel GMH6 2本（東洋曹達製）  
試料溶液 : 0.5%のTHF溶液  
溶液注入量 :  $20 \mu\text{l}$   
検出装置 : 屈折率検出器

【0017】実施例1

冷却管およびダブルヘリカルリボン攪拌機付き $1000$ リットル反応槽（以後反応槽1という）中にキシレン $64 \text{ kg}$ を仕込んだ後、 $200^\circ\text{C}$ に加熱し、その中にスチレン $400 \text{ kg}$ およびジ- $t$ -ブチル- $\alpha$ -オキサイド $12.1 \text{ kg}$ を $3$ 時間かけて滴下し、さらに同温度で $1$ 時間反応させて、重量平均分子量 $4200$ の樹脂（p-1）のキシレン溶液（a-1） $476.1 \text{ kg}$ を得た。該（a-1）にキシレン $80 \text{ kg}$ を加えた後、系内温度を $60^\circ\text{C}$ に保ち、攪拌しながら、懸濁重合法で得られた重量平均分子量 $85$ 万の粒状のスチレン/アクリル酸n-ブチル（重量比 $80/20$ ）共重合体（a-2） $171.4 \text{ kg}$ を $1$ 時間かけて投入し均一に溶解した。次に反応槽1中を窒素ガスで置換し、常圧で $180^\circ\text{C}$ まで昇

$5 \text{ Torr}$ 未満にするためには、大がかりな減圧装置が必要となり、 $50 \text{ Torr}$ を超えると、脱揮時間が長くなり樹脂の品質低下をまねき好ましくない。減圧状態を維持する時間は通常 $15 \sim 120$ 分である。

【0014】本発明の方法により脱揮された樹脂中の残存单量体の含有量は、通常 $200 \text{ ppm}$ 以下であり、好ましい条件を選択することにより $100 \text{ ppm}$ 以下とすることも可能である。

【0015】

【実施例】以下、実施例により、本発明をさらに説明するが、本発明はこれに限定されるものではない。なお、以下において%は重量%を示す。

【0016】測定に用いた装置、条件および方法は下記の通りである。

を精秤し、 $150^\circ\text{C}$ の循風乾燥機に $45$ 分間静置した後取り出し、乾燥残渣を精秤し下記計算式により求めた。

$$\text{揮発分 (\%)} = (1 - \text{乾燥残渣重量} / \text{サンプル重量}) \times 100$$

温し、次いで温度を $180^\circ\text{C}$ に保ったまま減圧状態にして揮発分を溜去し、樹脂（A-1）を得た。このものの揮発分は $0.9\%$ であった。次いで槽内を密閉にし、該（A-1）中に水蒸気を $5 \text{ kg/cm}^2$ Gとなるまで圧入した。攪拌下で、加圧状態を $30$ 分間維持した後、圧力が $20 \text{ Torr}$ になるまで減圧状態を保った。この水蒸気導入、減圧の操作を $3$ 回繰り返して樹脂（P-1）を得た。水蒸気を加え始めてから取り出しまでに要した時間は $5$ 時間であった。残存单量体（スチレン）の含量は $60 \text{ ppm}$ であった。

【0018】実施例2

反応槽1中にキシレン $64 \text{ kg}$ を仕込んだ後、 $200^\circ\text{C}$ に加熱し、その中にスチレン $342.4 \text{ kg}$ にテレフタル酸とビスフェノールAエチレンオキサイド $2$ モル付加

物の重縮合で得られた数平均分子量2500のポリエス  
テル樹脂（P E - 1）40Kgと（P E - 1）の末端の  
片方にメタクリロイルイソシアネートを反応したポリエ  
ステル樹脂（P E - 2）17.2Kgを溶解させた混合  
物およびジーエーブチルーバーオキサイド9.4Kgを  
3時間かけて滴下し、さらに同温度で1時間反応させ  
て、重量平均分子量4200の樹脂（P - 2）のキシレ  
ン溶液（a - 3）473Kgを得た。該（a - 3）中に  
キシレン80Kgを加えた後、系内温度を60℃に保  
ち、攪拌しながら、（a - 2）171.4Kgを1時間  
かけて投入し均一に溶解した。次に反応槽1中を窒素ガ  
スで置換し、常圧で180℃まで昇温し、次いで温度を  
180℃に保ったまま減圧状態にして揮発分を溜去し樹  
脂（A - 2）を得た。このものの揮発分は0.3%であ  
った。次いで槽内を密閉にし、該（A - 2）中に水蒸気を  
7Kg/cm<sup>2</sup>Gとなるまで圧入した。加圧状態を4  
0分間維持した後、圧力が20Torrになるまで減圧  
状態を保った。この水蒸気導入、減圧の操作をもう一度  
繰り返し樹脂（P - 2）を得た。水蒸気を加え始めてか  
ら取り出しまでに要した時間は3時間であった。残存ス  
チレンの含量は70ppmであった。

#### 【0019】比較例1

実施例1と同様にして得た樹脂（A - 1）を180℃で  
そのまま減圧状態を保ち、脱揮を行った。減圧状態での  
脱揮時間が8時間目に、残存スチレンの含量は450p  
pmに到達したが、それ以降は樹脂が分解を起こし、1  
3時間目には未反応スチレンの含量は600ppmに増  
加した。

#### 【0020】比較例2

実施例1と同様にして得た樹脂（A - 1）を140℃に  
保ち、減圧操作を行い脱揮を行った。減圧状態での脱揮  
時間が15時間目に揮発分が0.4%にまで減少した  
が、20時間以上脱揮操作を行っても揮発分は0.4%  
以下にならなかった。

#### 【0021】

【発明の効果】本発明の方法により、残存単量体含量の  
少ない樹脂を品質低下をおこすことなく、従来の方法に  
比べ極めて短時間で製造することが可能になった。ま  
た、本発明の方法は電子写真用トナー・バインダーだけ  
でなく粘着剤、食品用トレーに用いる樹脂等のビニル系單  
量体の重合体を主体とする樹脂の製造における残存モノ  
マー等の脱揮方法としても有効である。